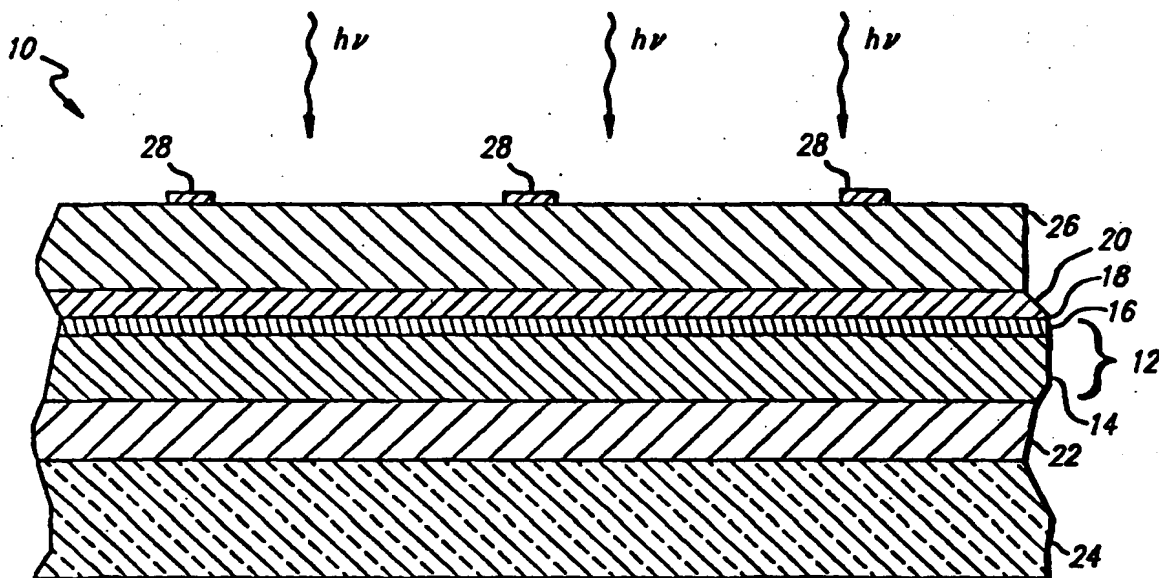




INTERNATIONAL APPLICATION PUBLISHED UNDER THE PATENT COOPERATION TREATY (PCT)

<p>(51) International Patent Classification ⁵ : H01L 31/18, 31/032, C30B 29/46</p>	<p>A1</p>	<p>(11) International Publication Number: WO 94/27328 (43) International Publication Date: 24 November 1994 (24.11.94)</p>
<p>(21) International Application Number: PCT/US94/04245 (22) International Filing Date: 18 April 1994 (18.04.94) (30) Priority Data: 08/058,404 7 May 1993 (07.05.93) US (71) Applicant: SIEMENS SOLAR INDUSTRIES INTERNATIONAL, INC. [US/US]; 4650 Adohr Lane, Camarillo, CA 93010 (US). (72) Inventors: ERMER, James, H.; 918 E. Tujunga Boulevard, Burbank, CA 91501 (US). TARRANT, Dale, E.; 3900 Calle Alta Vista, Newbury Park, CA 91320 (US). (74) Agents: BOLES, Donald, M. et al.; Siemens Corporation, Intellectual Property Dept., 186 Wood Avenue South, Iselin, NJ 08830 (US).</p>		<p>(81) Designated States: FI, JP, European patent (AT, BE, CH, DE, DK, ES, FR, GB, GR, IE, IT, LU, MC, NL, PT, SE). Published With international search report.</p>

(54) Title: PROCESS FOR AT LEAST PARTIALLY CONVERTING SEMI-CONDUCTOR FILMS OF THE I-III-VI₂-TYPE



(57) Abstract

A compound semiconductor film of the I-III-VI₂ type is exposed to a substance containing at least one additional element chosen from the chemical groups I, III and VI and is heated to a preselected temperature in the presence of the substance to exchange the additional element for at least a portion of one or more of the original constituent elements of the film. The result is a second compound semiconductor of the same type but having a different composition.

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**PROCESS FOR AT LEAST PARTIALLY CONVERTING
SEMI-CONDUCTOR FILMS OF THE I-III-VI₂ TYPE**

BACKGROUND OF THE INVENTION

The present invention relates generally to a process
5 for forming compound semiconductors and, more particularly,
to a process for at least partially converting compound
semiconductor films of the I-III-VI₂ type to semiconductors
of the same type with different composition.

Thin film I-III-VI₂ absorbers, such as CuInSe₂, are
10 promising materials for high power, low cost photovoltaic
applications. Because bandgaps for I-III-VI₂ absorbers range
from below one electron volt (ev) for CuInTe₂ to above 2.5 ev
for AgGaS₂, it is possible to optimize such materials by
carefully controlling their chemical compositions. Both the
15 bandgap and lattice constants of such materials can be
adjusted by changing the relative amounts of their
constituent elements, permitting I-III-VI₂ absorbers to be
used in both single junction and tandem junction
photovoltaic modules.

20 The concept of controlling the makeup of a I-III-VI₂
absorber by varying its chemical makeup is disclosed in the
following publications: N. Roy, et al. "The Diode Current
Mechanism in CuInSe₂/(CdZn)S Heterojunctions", Proceedings of
the 20th IEEE Photovoltaic Specialists Conference, September
25 26-30, 1988, pp 1618-1623; J.R. Tuttle, "Experiments on the
modification of the Bi-layer Structure in CdS/CuInSe₂
Devices", Proceedings of the 20th IEEE Photovoltaic
Specialists Conference, 1988, pp 1525-1530; G.B. Turner et
al., "Band Discontinuity and Bulk vs. Interface
30 Recombination in CdS/CuInSe₂ Solar Cells", Proceedings of the
20th IEEE Photovoltaic Specialists Conference, 1988, pp
1457-1460; R.J. Schwartz, "The Use of CuIn_{1-x}Ga_xSe₂ Layers to
Improve the Performance of CuInSe₂ Cells", Proceedings of the
21st IEEE Photovoltaic Specialists Conference, 1990, pp 570-
35 574; J.J. Loferski et al., "Investigation of Thin Film

Cadmium Sulfide/Mixed Copper Ternary Heterojunction Photovoltaic Cells", 13th IEEE Photovoltaic Specialists Conference, 1978, pp 190-194; J.R. Tuttle et al., "Physical, Chemical and Structural Modifications to Thin-Film CuInSe₂-
5 Based Photovoltaic Devices", 22nd IEEE Photovoltaic Specialists Conference, 1991, pp 1062-1067.

The foregoing references describe or suggest that the composition of a "multinary" semiconductor, i.e., a compound semiconductor having at least three constituent elements,
10 can be altered by incorporation of gallium, sulfur or other suitable elements in the absorber layer to raise the bandgap of the material and thereby raise the open circuit voltage of a resulting device. In each case, however, the composition of the compound semiconductor is determined by
15 the materials included at the time the compound is initially formed. Unfortunately, substitution of one constituent element for another in the process of formation can have a deleterious effect on certain properties of the resulting film, including its grain structure and uniformity. For
20 example, the inclusion of relatively high amounts of sulfur in copper indium diselenide and other multinary compounds tends to make the deposited films nonuniform over their surface. While the reasons for this are not entirely understood, the problem may result from differences in the
25 crystal growth mechanisms caused by the addition of sulfur.

Therefore, it is desirable in many applications to provide a process for forming multinary semiconductor compounds which are uniform over a large area and have improved physical structures.

30 SUMMARY OF THE INVENTION

The process of the present invention is capable of producing multinary semiconductors having a wide variety of constituents and composition profiles, including graded absorber regions, with high film uniformity. It is possible
35 according to the invention to convert part or all of what will later be the absorber layer without affecting the

remainder of the semiconductor film. Thus, the advantageous properties of a sulfur-rich region can be obtained on a selective basis in the absorber.

The foregoing advantages are achieved by: depositing or
5 otherwise providing a film including a first compound semiconductor having constituent elements chosen from each of the chemical groups I, III and VI; exposing at least one surface of the film to a substance containing at least one additional element chosen from the chemical groups I, III
10 and VI; and heating the film to a preselected temperature in the presence of that substance to cause the additional element to be exchanged for at least a portion of one or more of the constituent elements of the film; whereby the first compound semiconductor is at least partially converted
15 to a second compound semiconductor of different composition. The additional element can be a group I element, such as silver, a group III element, such as gallium; a group VI element, such as sulfur, or a combination of such elements. In one embodiment, the additional element is introduced in
20 the form of a gas. The additional element can be sulfur introduced in the form of hydrogen sulfide gas.

An important feature of the present invention is the fact that conversion takes place after the first I-III-VI₂-type compound semiconductor film is formed. Additional
25 elements enter the film during heat treatment and substitute themselves for constituent elements of the same chemical group, altering the composition and material properties of the affected region. The result of the process can be a partial conversion to a given depth of the film, possibly
30 resulting in a quaternary or other multinary compound, or may extend throughout the film such that the film is fully converted to a different semiconductor material. The limited conversion process is particularly well-suited for creating graded absorber layers which increase the open
35 circuit voltage of a resulting photovoltaic cell without unduly reducing short circuit current.

BRIEF DESCRIPTION OF THE DRAWINGS

The above and other features of the present invention may be more fully understood from the following detailed description, taken together with the accompanying drawings, wherein similar reference characters refer to similar elements throughout and in which:

FIGURE 1 is a schematic representation of a photovoltaic cell constructed from a I-III-VI₂-type semiconductor film formed in accordance with an illustrative embodiment of the present invention;

FIGURE 2 is schematic representation of a portion of the photovoltaic cell of FIGURE 1 in the process of formation;

FIGURE 3 is a simplified block diagram of an illustrative form of the process of the present invention;

FIGURE 4 is a graph showing the results of an Auger depth profile of an absorber structure of the type illustrated in FIGURE 2, in which the composition of the absorber is graded to achieve a high efficiency;

FIGURE 5 is a graph of the current voltage characteristic of a photovoltaic cell of the type illustrated in FIGURE 1, including calculated values for open circuit voltage (V_{oc}), short circuit current (J_{sc}), fill factor (FF) and efficiency (Eff);

FIGURE 6A is a graph illustrating the relationship between efficiency and sulfur content (in percent) for a photovoltaic cell of the type depicted in FIGURE 4;

FIGURE 6B is a graph showing the dependence of open circuit voltage (V_{oc}) as a function of relative sulfur content;

FIGURE 6C is a graph showing the dependence of short circuit current (J_{sc}) on relative sulfur content; and

FIGURE 7 is a graph of the spectral response of a copper-multinary structure having a graded absorber, as compared to copper-multinary devices having homogeneous high and low bandgap absorbers, respectively.

DESCRIPTION OF THE PREFERRED EMBODIMENT

Referring now to the drawings, specifically FIGURES 1 and 2, a photovoltaic device 10 constructed according to an illustrative embodiment of the present invention has a p-type compound semiconductor layer 12 made up of a bulk region 14 and a converted surface region 16. In the illustrated embodiment, the converted surface region 16 includes part or all of the "absorber" region (not separately shown) of the semiconductor layer 12, and forms a heterojunction 18 with an n-type semiconductor layer 20, such as cadmium sulfide (CdS) or zinc oxide (ZnO). The compound semiconductor layer 12 is formed on a back contact 22 which is a thin film of molybdenum (Mo) or other suitable metal deposited on a substrate 24. Contact to the n-type layer 20 is made by a transparent conductive oxide layer 26 and, in some device configurations, a plurality of conductive grid lines 28. Thus, light (hv) enters the device through the transparent oxide layer 26 and passes through the n-type layer 20 and into the p-type compound semiconductor layer 12. Virtually all of such light is absorbed within the absorber portion of the p-type layer 12, which extends up to about 10,000 angstroms into the p-type layer.

The "converted" surface region can extend through part or all of the absorber region, as described in more detail below. The light absorbed in this region generates free carriers which are separated by the built-in electric field resulting from the p-n heterojunction 118, causing current to flow through an external circuit connected between the back contact 22 and the conductive grid lines 28. The basic components of the photovoltaic device 10 and known methods for fabricating them are described in U.S. Patent No. 4,798,660, issued January 17, 1989 to Ermer et al., and U.S. Patent No. 5,045,409, issued September 3, 1991 to Eberspacher et al., the specifications of which are incorporated herein by reference for all purposes.

FIGURE 2 illustrates a portion of the photovoltaic device 10 at the stage in its fabrication when the surface region 16 of the semiconductor layer 12 is converted to a different compound semiconductor by the process of the present invention. Thus, the p-type layer 12 is formed on the back electrode 22 prior to conversion. This can take place either just prior to conversion or far in advance of it. Either way, the upper surface of the layer 12 is eventually exposed to a substance containing at least one additional element chosen from the chemical Groups I, III and VI and heated to a preselected temperature in the presence of the substance to cause at least a portion of one of the constituent elements of the original layer to be displaced by the additional element.

The number of atoms entering the layer 12 and the depth to which they penetrate (indicated by a broken line in FIGURE 2) are dependent on the characteristics of the additional element and the substance containing it, as well as the concentration of the substance and the temperature and duration of the heat treatment step. Although the entire layer 12 can be converted by the process of the invention, if desired, it is desirable in most cases to convert something less than the entire absorber region. This creates a graded concentration profile which provides a high bandgap and the attendant high open circuit voltage (V_{oc}). When the I-III-VI₂ semiconductor layer 12 is formed of CuInSe₂, and the additional element is sulfur or gallium, the conversion may also neutralize "dangling bonds" at the surface region in much the same way that hydrogen passivates dangling bonds in thin film silicon-containing alloys.

The process of the invention is illustrated in its simplest form in the flow chart of FIGURE 3, wherein the I-III-VI₂ semiconductor layer 12 is deposited at S10, is exposed at its upper surface to an additional Group I, III or VI element, such as gallium or sulfur, at S12, and is annealed in the presence of the additional element at S14 to exchange the additional element with the corresponding

constituent element of the original film. As described above, the step S10 can include formation of the I-III-VI₂ semiconductor just before the exchange takes place, or the original layer can be formed well in advance of the conversion. Step S12 can be accomplished by exposure of the film to a gas, such as hydrogen sulfide, which contains the additional element. Alternatively, the additional element can be applied in any other convenient way, such as by depositing a layer of solid material on the upper surface of the semiconductor layer 12, exposing the film to a vapor of the material itself, or applying an organic compound, such as a mercaptan, in the case of sulfur. All that is required is that the element be available to enter the film in place of one of the constituents of the original film when the composite structure is subjected to heat at S14.

In a preferred embodiment in which the semiconductor layer 12 is CuInSe₂ and sulfur is introduced from hydrogen sulfide gas placed in contact with the layer 12, the concentration of sulfur in the atmosphere is preferably between 5 percent and 50 percent of the gaseous atmosphere, the remainder being nitrogen, argon or other suitable carrier gas. The concentration of hydrogen sulfide is most preferably approximately 30 percent for purposes of the invention. The temperature of conversion is preferably at least 450 degrees in order to dissociate the hydrogen sulfide gas and release sulfur into the layer 12, and more preferably between approximately 475 and 550 degrees C. The sulfidation process typically lasts between 5 and 50 minutes, and most preferably approximately 20 minutes. Under these circumstances the depth of sulfur within the layer 12 is typically between 100 and 5000 angstroms, most preferably approximately 1500 angstroms, to provide a graded bandgap structure.

FIGURE 4 illustrates an Auger depth profile of the structure of FIGURE 2 after partial conversion of the layer 12. Thus, the time designated "0" at the left hand side of the graph indicates the concentrations of elements at the

upper surface of the region 12, as detected by Auger analysis. It can be seen that the concentrations of sulfur and selenium are approximately equal, making the material a "sulfoselenide" at its surface. Extending downwardly from the surface (moving from left to right on the time scale of FIGURE 4), the sulfur concentration is graded rapidly down and the selenium concentration increases rapidly until the sulfur signal essentially disappears (approximately 20 minutes into the analysis). Thus, sulfur is exchanged for selenium near the surface, raising the bandgap and possibly passivating any dangling bonds. The resulting body is much more uniform and much higher in quality than when sulfur is introduced during layer formation as disclosed in the prior art.

FIGURE 5 is the measured current-voltage characteristic of the graded cell of FIGURE 4, in which the open circuit voltage (V_{oc}) and the short circuit current (J_{sc}) yield an efficiency of 15.1 percent. The significance of this in comparison to a similar cell containing sulfur homogeneously throughout its thickness is illustrated in the graph of FIGURE 7. FIGURE 7 shows that the graded sulfur device has a quantum efficiency similar to that of a cell that does not contain sulfur, and much greater than a homogeneous $Cu(InGe)(Se, S_2)$ cell.

The optimal sulfur content within the absorber region for a particular temperature of heat treatment can be obtained from FIGURES 6A, 6B and 6C, which illustrate the efficiency, open circuit voltage and short circuit current, respectively, at relative sulfur contents ranging from approximately 25 percent up to 100 percent. It should be noted in connection with these graphs, however, that the sulfur content for these purposes is defined as the concentration of sulfur in an absorber normalized to the absorber with the highest measured sulfur concentration.

Thus, 100 percent total sulfur concentration does not represent stoichiometric $CuInS_2$. Keeping this in mind,

FIGURES 6A-6C show that the optimal relative sulfur content is between 40 and 55 percent.

From the above, it can be seen that the disclosed process for conversion of I-III-VI₂-type semiconductors enables higher quality and/or more uniform layers to be deposited and permits the formation of high efficiency photovoltaic devices having high open circuit voltage.

While the preferred embodiment has been described and illustrated, various substitutions and modifications may be made thereto without departing from the scope of the invention. For example, the process of the present invention is applicable to the formation of a wide variety of I-III-VI₂-type semiconductor compounds, including by way of example, compounds in which the group I element is copper and/or silver, the group III element is indium and/or gallium, and the group VI element is selenium and/or sulfur. Such compounds can also include one or more other elements, such as those of chemical group IV, in addition to the group I, III, VI components without departing from the scope of the invention. Accordingly, it is to be understood that the present invention has been described by way of illustration and not limitation.

WHAT IS CLAIMED IS:

1. A process for at least partially converting a compound semiconductor film of the I-III-VI₂ type to a another compound semiconductor comprising:
 - 5 providing a film including a first compound semiconductor having constituent elements chosen from each of the chemical groups I, III and VI;
exposing at least one surface of the film to a substance containing at least one additional element chosen
10 from the chemical groups I, III and VI; and
heating the film to a preselected temperature in the presence of said substance to exchange said at least one additional element for at least a portion of one or more of the constituent elements of said film;
15 whereby the first compound semiconductor is at least partially converted to a second compound semiconductor of different composition.
2. The process of claim 1 wherein:
the step of providing said film comprises forming said
20 film on a substrate.
3. The process of claim 1 wherein:
a graded bandgap is created in the compound semiconductor film as a result of said at least partial conversion.
- 25 4. The process of claim 1 wherein:
said at least one additional element is chosen from the chemical group VI.
5. The process of claim 4 wherein:
the first compound semiconductor includes selenium; and
30 said at least one additional element is sulfur.
6. The process of claim 5 wherein:

said preselected temperature is greater than 450 degrees C.

7. The process of claim 6 wherein:
said preselected temperature is at least approximately
5 500 degrees C.

8. The process of claim 1 wherein:
the process of exposing at least one surface of the
film to at least one additional element comprises exposing
said surface to a gas containing said at least one
10 additional element.

9. The process of claim 8 wherein:
said gas contains hydrogen.

10. The process of claim 9 wherein:
the first compound semiconductor includes selenium;
15 said at least one additional element is sulphur; and
said gas is hydrogen sulphide.

11. The process of claim 10 wherein:
the step of providing said film comprises forming the
film on a substrate by a process in which at least one layer
20 containing elements chosen from each of the chemical groups
I and III is heat treated in the presence of hydrogen
selenide within a reaction chamber; and
the steps of exposing the film to a substance and
heating the film to a preselected temperature take place in
25 said chamber, as well.

12. The product formed by the process of claim 1.

13. A process for at least partially converting a
copper-multinary semiconductor film to a another copper-
multinary semiconductor comprising:

providing a film including a first copper-multinary semiconductor having constituent elements chosen from each of the chemical groups I, III and VI;

5 exposing at least one surface of the film to a substance containing at least one additional element chosen from the chemical groups I, III and VI; and

heating the film to a preselected temperature in the presence of said substance to exchange said at least one additional element for at least a portion of one or more of
10 the constituent elements of said film;

whereby the first copper-multinary semiconductor is at least partially converted to a second copper-multinary semiconductor of different composition.

14. The process of claim 13 wherein:
15 the first compound semiconductor includes selenium; and said at least one additional element includes sulfur.

15. The process of claim 13 wherein:
the first compound semiconductor includes indium; and said at least one additional element includes gallium.

20 16. The process of claim 13 wherein:
the first compound semiconductor includes indium and selenium; and
said at least one additional element includes gallium and sulphur.

25 17. A process for at least partially converting a compound semiconductor film of the Cu-In-Se₂ type to a another compound semiconductor comprising:

providing a film including a first compound semiconductor containing Cu, In and Se;
30 exposing at least one surface of the film to a substance containing at least one additional element chosen from the chemical groups I, III and VI; and

heating the film to a preselected temperature in the presence of said substance to exchange said at least one additional element for at least a portion of one or more of the constituent elements of said film;

- 5 whereby the first compound semiconductor is at least partially converted to a second compound semiconductor of different composition.

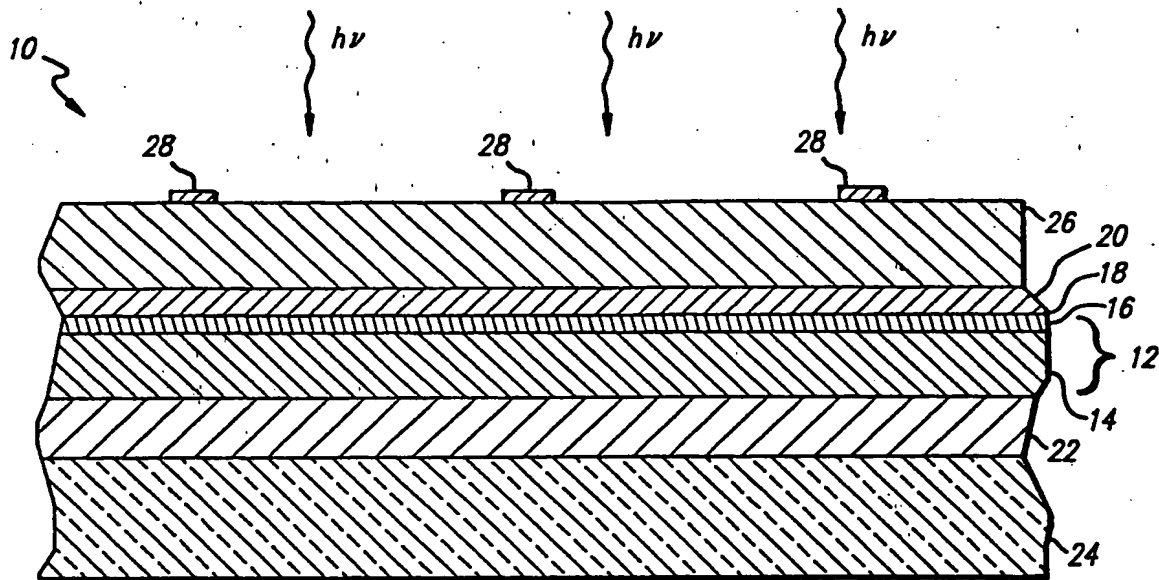


FIG. 1

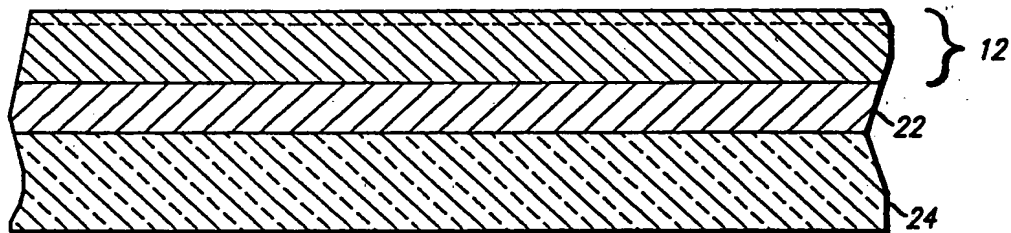
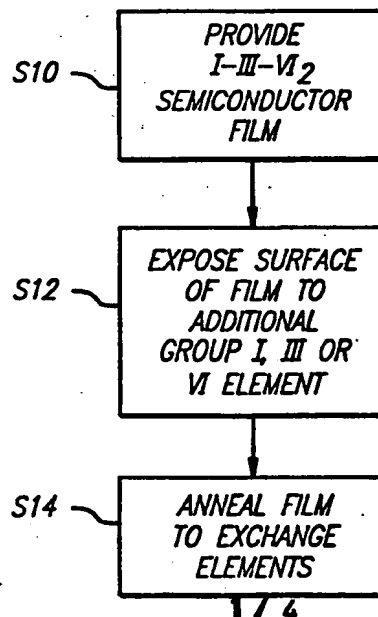


FIG. 2

FIG. 3



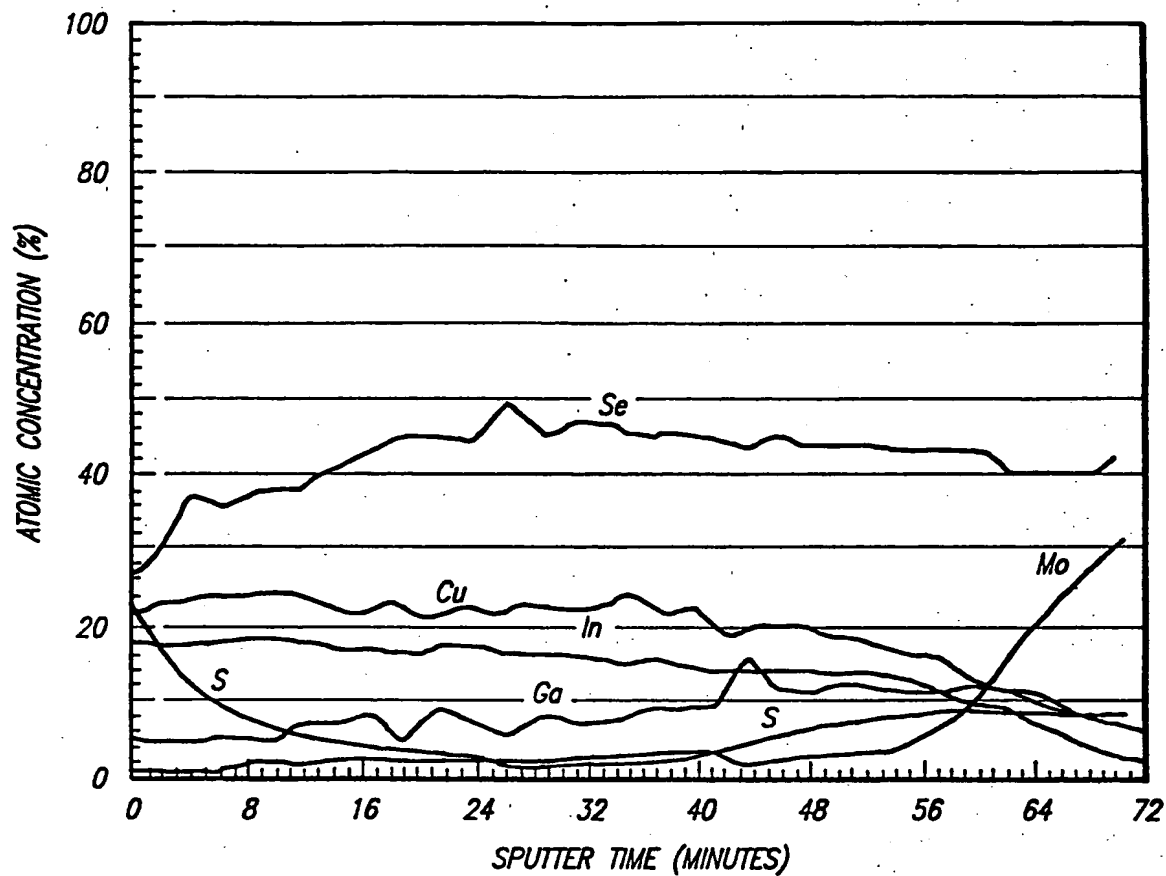


FIG. 4

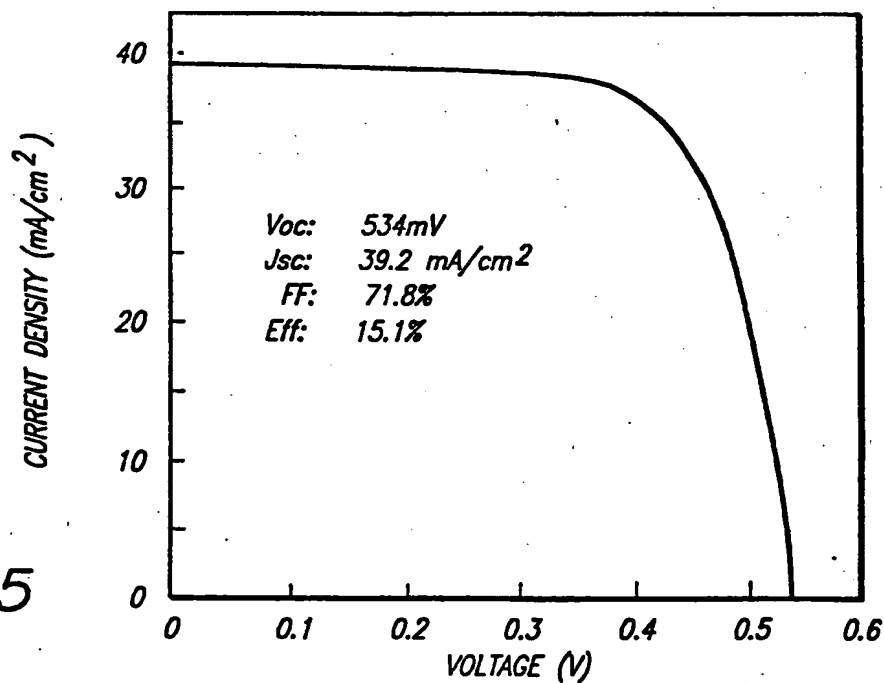


FIG. 5

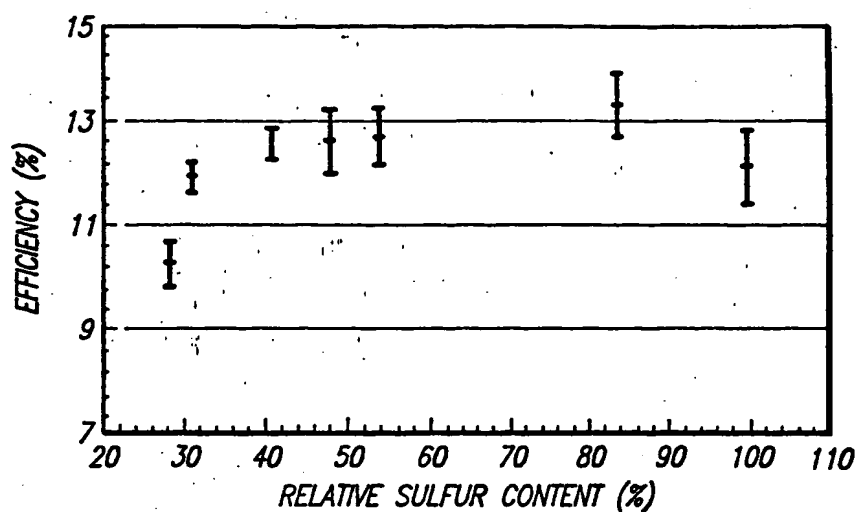


FIG. 6a

FIG. 6b

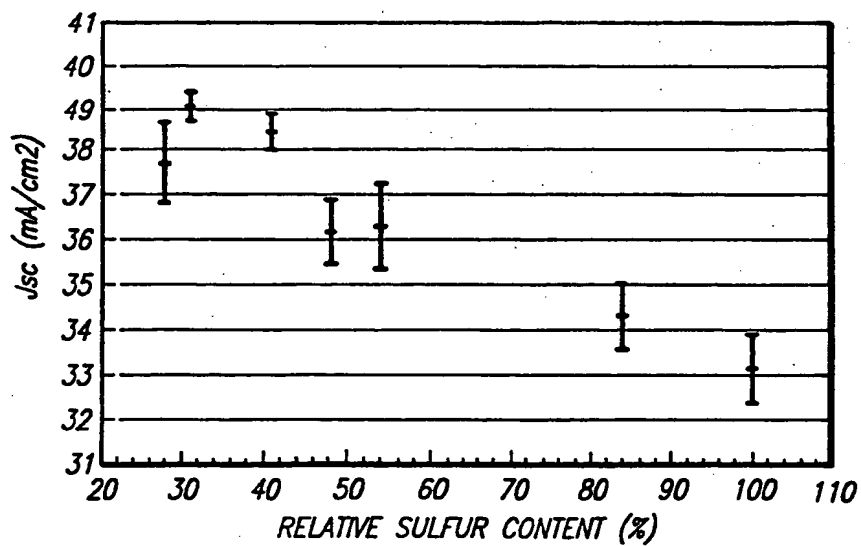
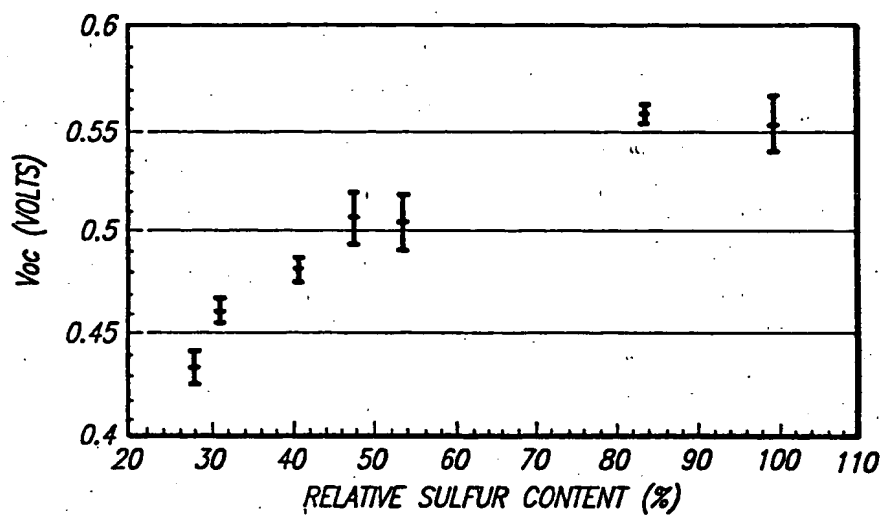


FIG. 6c

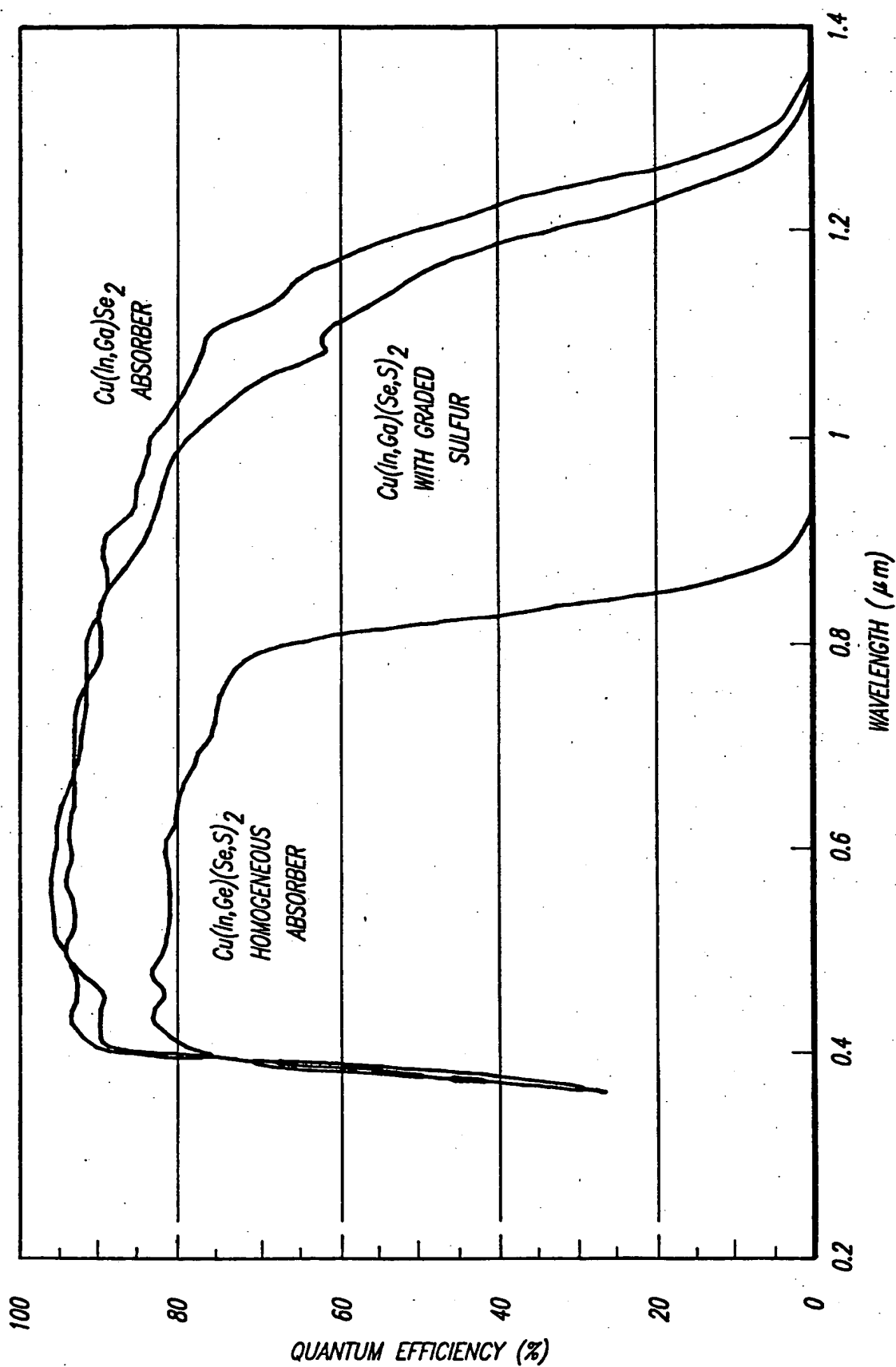


FIG. 7

INTERNATIONAL SEARCH REPORT

International Application No

PCT/US 94/04245

A. CLASSIFICATION OF SUBJECT MATTER

H 01 L 31/18, H 01 L 31/032, C 30 B 29/46

According to International Patent Classification (IPC) or to both national classification and IPC ⁵

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)

H 01 L, C 30 B, C 23 C,

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practical, search terms used)

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category *	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	EP, A2/3, 0 318 315 (ATLANTIC RICHFIELD) 31 May 1989 (31.05.89), column 2, lines 15-32.	1-5, 8-17
X	TWENTIETH IEEE PHOTOVOLTAIC SPECIALISTS CONFERENCE - 1988 VOLUME II, September 1988, J.R. TUTTLE et al. "Experiments on the Modification of the Bi-Layer Structure in Cds/CuInSe ₂ Devices", pages 1525-1530, especially page 1528, left hand column, paragraph 1-4 (cited in the application).	1, 2, 6, 12, 13
A	TWENTY SECOND IEEE PHOTO-VOLTAIC SPECIALISTS	1-17



Further documents are listed in the continuation of box C.



Patent family members are listed in annex.

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Date of the actual completion of the international search

17 August 1994

Date of mailing of the international search report

07.09.94

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HEINICH e.h.

INTERNATIONAL SEARCH REPORT

-2-

International Application No

PCT/US 94/04245

C.(Continuation) DOCUMENTS CONSIDERED TO BE RELEVANT		
Category *	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
	<p>CONFERENCE - 1991, VOLUME II, October 1991, J.R. TUTTLE et al. "Physical, Chemical and Structural Modifications to Thin-Film CuInSe₂-based Photovoltaic Devices", pages 1062-1067, especially page 1062, right hand column, paragraph 3.</p> <p>--</p>	
A	<p>THIRTEENTH IEEE PHOTOVOLTAIC SPECIALISTS CONFERENCE - 1978 June 1978, J.J. LOFERSKI et al. "Inves- tigation of Thin Film Cadmium, Sulfide/Mixed Copper Ternary Heterojunction Photovoltaic Cells", pages 190-194, especially pages 190,191; right hand columns.</p> <p>--</p>	1,12, 13,17
A	<p>EP, A1, 0 195 152 (ATLANTIC RICHFIELD) 24 September 1986 (24.09.86), claims 1,11-14,18-21,25; page 3, line 10 - page 4, line 29.</p> <p>--</p>	1-17
A	<p>US, A, 4 335 266 (MICKELSEN) 15 June 1982 (15.06.82), fig. 4; column 13, line 10 - column 14, line 2.</p> <p>----</p>	1-17

ANHANG

ANNEX

ANNEXE

zum internationalen Recherchen-
bericht über die internationale
Patentanmeldung Nr.

to the International Search
Report to the International Patent
Application No.

au rapport de recherche inter-
national relatif à la demande de brevet
international n°

PCT/US 94/04245 SAE 90340

In diesem Anhang sind die Mitglieder
der Patentfamilien der im obenge-
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Diese Angaben dienen nur zur Unter-
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This Annex lists the patent family
members relating to the patent documents
cited in the above-mentioned inter-
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In Recherchenbericht angeführtes Patentedokument in search report Document de brevet cité dans le rapport de recherche	Datum der Veröffentlichung Publication date Date de publication	Mitglied(er) der Patentfamilie Patent family member(s) Membre(s) de la famille de brevets	Datum der Veröffentlichung Publication date Date de publication
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